EXHIBIT A

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VINYL CHLORIDE MONOMER EMISSIONS
FROM THE POLYVINYL CHLORIDE PROCESSING INDUSTRIES

Report to
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina

II. POLYVINYL CHLORIDE MANUFACTURING: PROCESSES AND APPLICATIONS

A. GENERAL

Plastic products based on polyvinyl chloride (PVC) are among the oldest of the major plastic materials. The first commercial plant to make PVC resin was constructed in 1939, and consumption has now grown to over 4.5 billion pounds per year--the second largest plastic (after polyethylene) consumed in the United States. PVC is the most versatile type of synthetic resin produced and is used in more individual end products than any other type of plastic material. This versatility arises from the relatively low cost of PVC, its ease of fabrication, its solvent, weather and abrasion resistance, and the fact that its mechanical properties can be varied by proper adjustment of additives to yield products ranging from rigid, brittle materials to soft, rubbery ones.

There are three major processes in the conversion of vinyl chloride monomer to a finished polyvinyl chloride product: (1) polymerization of the monomer to the polymer; (2) compounding, or addition of additives to the polymer to yield the desired properties for handling the polymer and in the final product; and (3) fabricating, in which the compound is melted and then formed into the final shape required. Because of the wide variety of uses to which PVC is put, there is a considerable variety of polymerization processes, compounding operations and fabricating processes which must be used to arrive at the desired end properties. Figure II-1 presents a schematic of the types of polymerization processes used to produce each end product. These processes are discussed in some detail in the following subsections.

PVC resins vary in molecular weight and in chemical composition. The molecular weight of most commercial PVC resins lies between 50,000 and 120,000 and most PVC resins are homopolymers made from vinyl chloride alone. About 15% of the vinyl chloride polymers are copolymers containing vinyl chloride and other monomers, with vinyl acetate being the most common comonomer. The processing and performance characteristics of PVC depend upon the nature of the polymer itself and on the additives used in the compound.

Although it is the purpose of this present program to assess vinyl chloride monomer emissions only from the compounding and fabricating steps of this process, the details of the polymerization processes also impact on the monomer emitted. The different polymerization processes result in different amounts of residual monomer remaining in the raw resins, which may later be emitted during fabrication operations.

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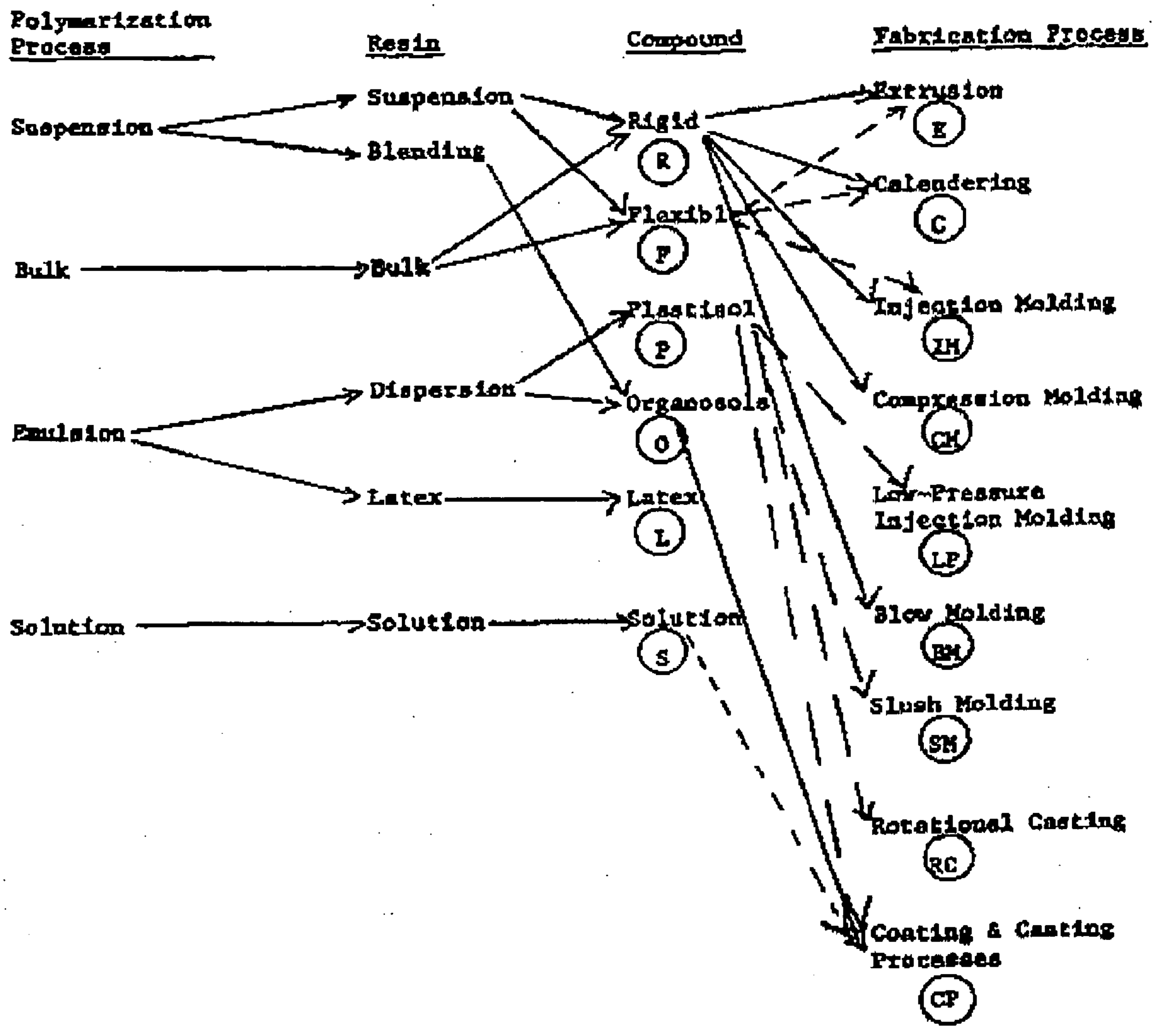

Figure II-la. Polyvinyl Chloride Manufacturing Processes

End Product	Fabrication Process	Compound
Pipe & Conduit	E	R
Panel & Siding	E	R
Flooring	CP, C	P, F
Upholstery	CP, C	P, F
Pipe Fittings	IM	R
Lighting Fixtures	E	R
Film (Packaging)	E, CP, C	F, S, R
Sheet (Packaging)	C, E	R
Rainwater Systems	E	R
Bottles	BM	R
Weather Stripping	E	F
Wire & Cable	E	F
Baby Pants	C	F
Footwear	LP, IM, SM, CP, C	P, F
Outerwear	CP, C	P, F

Windows	E	R
Hose	E	F
Phonograph Records	CM	R
Toys	RC, IM, LP	P, F. R
Auto Mats	CP	P
Auto Tops	C, CP	P, F
Medical Tubing	E	F
Tool Handles	CP	P
Credit Cards	E	R
Wallcoverings	C	F
Can Coating	CP	S, O
Exterior Paint		L
Closure Gaskets	LP	P

Figure II-lb. Polyvinyl Chloride Manufacturing Processes
(For key to processes and compounds see Figure II-la above)

II-3

B. POLYVINYL CHLORIDE POLYMERIZATION PROCESSES

1. Description of Processes
There are four commercial processes currently employed in the U.S. for the manufacture of PVC resin: suspension, emulsion, bilk, and solution polymerization. All four processes are based on free-radical polymerization of vinyl chloride monomer, using initiators such as organic peroxides. The choice of polymerization method depends on the ultimate application of the resin and the economics of the processes.

a. Suspension Polymerization

Suspension polymerization is the most commonly used process in the U.S. today, accounting for about 80% of PVC production. This process can be used to prepare both homopolymers and copolymers of a variety of molecular weights. In the suspension process vinyl chloride monomer is suspended in water with a small amount of a suspending agent. The molecular weight of the resulting polymer is generally controlled by the reaction temperature and by the addition of modifiers. After completion of the polymerization reaction, the solid polymer, which is in the form of fine beads, is recovered by centrifugation and drying. Depending upon the ultimate application, the product may be sold as (1) an unstabilized polymer, usually in the powder form as it is obtained from the reactor; (2) a dry powder blend with additives and/or colorants; or (3) a pelletized compound. Suspension resins are used for both rigid and flexible formulations.

b. Emulsion Polymerization

About 11% of the PVC resin produced in the United States in 1974 was produced by emulsion polymerization, which is basically very similar to the suspension process, except that relatively large amounts of emulsifying agents are used. This process produces resins with a very small particle size and typically of higher molecular weight than the suspension resins. To maintain the small particle size, emulsion resins are usually dried using a spray drying technique. (Complete removal of the emulsifiers is never achieved in resins produced by this process so that products requiring high clarity, for example, packaging film or very low water adsorption, such as wire insulation, cannot be produced from emulsion resins. The resulting powders, which are called paste resins or dispersion resins are sold either to independent compounders or to fabricators.

In the United States all plastisols are made from dispersion resins, primarily homopolymers. About lox of the polymers made by the emulsion process--or a total of about 50 million pounds of PVC in 1974--were sold as latices for coating app applications; all of these are copolymers.

c. Bulk Polymerization

Bulk polymerization is a relatively new process in the United States. It was developed in France (by Pechiney) and is used by Hooker Chemical Corporation,

the Goodyear Tire & Rubber Company, and the B.F. Goodrich Company. About 6% of the PVC resins produced in the U.S. in 1974 was made this way.

In this process the monomer is polymerized in the absence of solvent. The reactors are specially designed to handle bulk polyvinyl chloride at elevated temperatures.

These bulk polymers have several desirable features--high porosity (desirable in making flexible compound), clarity, and relatively uniform shape and size of the particles. They also have remarkably good heat stability and improved fusion properties, and can be processed with the ease of conventional vinyl chloride-vinyl acetate copolymers. Bulk-polymerized resins resemble the suspension resins and are used in the same applications.

d. Solution Polymerization

Although solution polymerization is over 40 years old, only about 3% of the PVC resins produced in the United States in 1974 were produced by this method. At present vinyl chloride solution polymerization is used only for the production of copolymers of vinyl chloride and vinyl acetate (usually containing 10-25x vinyl acetate). Union Carbide is currently the only U.S. producer of solution-polymerized resins.

In the solution process the monomers are dissolved in organic solvents such as n-butane or cyclohexane. The polymerization is carried out in an autoclave, and the polymer precipitates as the reaction proceeds. The resulting resins are usually dried and sold as powders or beads. Most solution process resins are sold to formulators who prepare solutions containing these resins for various coating applications.

2. Trends and Markets

Table II-1 shows the U.S. production of PVC resins in the last five years categorized by polymerization process. (Appendix Table A-I lists the major U.S. resin manufacturers.) As shown in Table II-1, in the period 1969-73, PVC production increased at an annual growth rate of about 11%.

Production growth slowed to about 7% last year. Most of this growth has been the production of suspension homopolymer resins. (Table II-1 resins made by the bulk process are included with the suspension resins.) Because of the improvement in the processibility of suspension and bulk hompolymers, the need for easier-processing copolymers has diminished over the past few years.

C. COMPOUNDING OF PVC RESINS

Pure polyvinyl chloride resin is usually unsatisfactory as a material for packaging, construction, upholstery, and many of the other applications for which it is used. Its brittleness, difficulty of processing, degradability, etc., require that the raw resin be "compounded" with a variety

TABLE II-1
U.S. PRODUCTION OF PVC RESINS
By Polymerization Process (MM Pounds)

	Suspension Homopolymers[a]	Suspension Copolymers	Dispersion Resins and Latex	Total
1969	2052	592	388	3032
1970	2232	519	364	3115
1971	2475	504	458	3437
1972	3149	559	550	4258
1973	3433	540	589	4562
1974[c]	3687	581	632[d]	4900
Annual Growth (%)				
1969-1973	13.8	-2.5	11.0	10.7
1974	7.3	7.6	7.3	7.5

[a] Includes polymers made by bulk process.
[b] Includes polymers made by solution process.
[c] Estimated by Modern Plastics, January, 1975.
[d] We estimate the production of dispersion resins in 1974 amounted to 475 MM lbs.

Source: Society of Plastics Industries, Annual Statistical Reports, and Modern Plastics, January, 1975, and ADL.

of additives in order to achieve the required properties. The concentration of additives in these compounds can vary from 3% to over 100% (based on the weight of resin). Four major categories of compounding are considered: (1) rigid PVC compounding; (2) flexible compounding; (3) compounding (or formulating) of plastisols and organosols; and (4) formulating of PVC solutions.

(1) Rigid Compounds

Rigid compounds, which are supplied as powders or pellets, contain from 80 to 97% PVC depending upon the end application. Three to five percent of an elastomeric product is often added as an impact modifier to rigid compounds used for pipe applications. Rigid compounds often require pigments such as titanium oxide in addition to lubricants and stabilizers.

Although most rigid compounds are homopolymers, some copolymers are also sold. These are usually lower

in molecular weight than the homopolymers, and contain vinyl acetate as the comonomer.

Dry blending is typically used to prepare rigid compounds of PVC in powder form. These powders are usually used to manufacture PVC pipe. Dry blend powders are economical, particularly if compounding is done directly in the polymerization vessel prior to discharging the resin. Robintech today manufactures a suspension resin which is compounded in the polymerization kettle and used to fabricate pipe, and which does not require further dry blend compounding.

(2) Flexible Compounds

Flexible PVC products require plasticizer to soften the hard resin; the types and concentration of plasticizers used are very varied. Flexible compounds are made by mixing the dry PVC resin with plasticizer and other additives, frequently followed by fusing and pelletizing of the compound. In these compounds, the dry resin accounts for 33-60% of the composition, with the plasticizers, fillers, antioxidants, lubricants, and other additives comprising the remainder. Resins used are primarily high-molecular-weight homopolymers; the molecular weight is usually higher than resins used in making rigid compounds. Resins for flexible compounds, like those for rigid compounds, are made by the suspension or bulk process.

(3) Plastisols and Organosols

Most flexible PVC coatings and a small fraction of flexible molded products are made from plastisols. These plastisols are dispersions of PVC resins in plasticizer with other compounding ingredients such as stabilizers, fillers, and pigments. Some plastisols are very thin liquids, and others are heavy, doughy pastes. The manufacture of plastisols requires PVC dispersion resins, which are made primarily by the emulsion process (although a very small percentage is produced by the solution process). Plastisols are made primarily from homopolymers.

Because the dispersion resins are more expensive than those made by the suspension process, small amounts of suspension resins are often added to lower the costs of a plastisol formulation. Suspension resins used for this application are called blending resins.

Organosols are similar in constitution to plastisols, except that they are thinned with solvents to control the viscosity for certain coating processes. Organosols are often used in coating processes, such as metal coating, where low viscosities are needed and where evaporation of the volatile thinner does not affect the appearance of the product.

Plastisols and organosols are not sold by the resin producers. They are sold either by an independent formulator or are prepared by the fabricator.

(4) Solutions

PVC solutions are also used for coating applications. Most PVC can coatings are formed from such solutions. Resins for this application are prepared primarily by solution polymerization although some are synthesized by the suspension polymerization process. Because the dispersing agents in suspension resins interfere with the properties of the solution, they must be removed after polymerization; otherwise, the coating resin will not

possess maximum clarity and water resistance properties.

Most PVC solution coating resins are copolymers, typically containing 3 to 161 vinyl acetate as the comonomer; copolymers with vinylidene chloride or vinyl ethers are also available.

Because of the limited solubility of vinyl copolymers, strong solvents such as ketones and esters are used by the formulators, as the base of PVC coating solutions.

D. FABRICATION PROCESSES

1. Types of Processes

PVC compounds, both flexible and rigid, are converted to end products by a number of processing techniques including extrusion, calendering, injection molding, blow molding and compression molding. Flexible compounds are usually processed at lower temperatures than rigid ones, because the increased plasticizer compound lowers the softening point of the resins. Plastisol processing techniques include coating, casting, slush molding, rotational moldings and low-pressure injection molding.

a. Extrusion

The basic machine is the extruder, which consists of a metal barrel, a closefitting internal screw(s) connected to a drive mechanism and a means for applying heat to the barrel in one or more zones. The process consists basically of mixing and melting a continuous stream of plastic and

pushing it through a specially designed orifice or die by the turning action of the screw(s). In general, the extruder is very versatile with respect to the type of materials it can process.

Extrusion is used for marking continuous lengths of profiles. (A "profile" varies only in two dimensions, as opposed to molded products which vary in three.) Major profile products include: film and sheet, wire coating, pipe rod, and siding. Both flexible and rigid PVC compounds in either powder or pellet form are used in this process; either suspension or bulk process resins may be used.

Wire and cable insulation accounts for a significant portion of the flexible compound that is extruded. In wire and cable coating, the compound is extruded around a continuous length of the wire or cable.

Typically, pelletized compound is used in this process. The concentration of plasticizer in the compound varies with the application. For example, communication wire contains about 60% PVC. Most fabricators in this segment of the industry do their own compounding, although a few purchase the compound.

Rigid pipe and tubing are formed as continuous extrusions through an annular die approximating the desired profile; cooling is usually effected by passing the extrudate through a water bath or trough. Pipe as large as one meter in diameter can be prepared this way.

Pipe extrusion requires the use of rigid compounds, containing 85 to 95% PVC. Most PVC resins used in pipe manufacture are compounded into powder blends by the pipe producer. However, Robintech sells pipe

compound made by the in-kettle-compounding process.

Siding, Rain Gutters and Other Special Profiles are made in a similar way to rigid pipe. However, because these profiles are somewhat more difficult to extrude than pipe, manufacturers use rigid compound in pellet form for these processes. This segment of the industry typically uses single-screw extruders and purchases the compound.

Flexible Profiles are extruded from flexible compounds and include such items as medical tubing, garden hose, gaskets, weather stripping, water-stop sheet, and cove base. Pelletized compound is used, typically containing about 60% PVC, with the remainder being plasticizers, pigments, and stabilizers. Major manufacturers of flexible profiles do their own compounding; smaller manufacturers usually purchase compound.

PVC film can be made either by extrusion or calendering. In the blown-film extrusion process, which is the preferred method for packaging films, pellets of homopolymer compound are melted and extruded through a die with a thin, annular opening to produce a thin-walled tube.

Shrink film is made by stretching the film either as it is made or in a subsequent stretching operation. Stretching introduces orientation (the alignment of polymer chains).

A small amount of film is produced by flat die (slit-die) extrusion. This involves extruding molten resin from an extruder through a wide slit die with adjustable lips into a cooling system. These films typically have a lower degree of orientation than the blown film.

Sheet products (films greater than 10 mils in thickness) are manufactured by the slit-die extrusion technique. Most sheet extrusion processes use rigid compounds, although some may contain up to 10% plasticizer, depending upon the exact physical requirements of the end application. Sheet compounds usually are made from homopolymers; both pellets and powders can be used. Most fabricators purchase sheet compound, but a few of the larger fabricators do their own compounding.

A large portion of the sheet products are used in construction applications. such as transparent corrugated sheets. Sheet is corrugated by passing it through forming rolls after extrusion. Rigid sheet is also used in various packaging applications.

b. Calendering

Calendering is used primarily in the production of flexible sheet although a small fraction of rigid sheet is produced by this method. Calendering is capable of producing high-quality material at very high rates of output. In this process, the compound is passed between a series of three or four large heated revolving rollers which squeeze the material into sheet or film. The thickness of the finished material is controlled by the space between the final rolls. The resulting surface of the film or sheeting may be smooth, matted., or embossed, depending on the surface of the final rollers.

Calendering also can be used to coat PVC onto textiles or other supporting materials. In applying a coating, the compound is passed between two top horizontal rollers on a calender, while the uncoated material is

passed between two bottom rollers. Finally, the substrate and film converge and are passed between a single set of rollers; the product emerges as a smooth film or sheet anchored to the substrate.- The alternative process to calender coating is post-calender laminating. In this process, the vinyl coating is prepared in advance and then laminated onto fabric by passing the two materials through pressure rolls.

Although the cost of the calender together with the auxiliary equipment is very high (a typical calender train costs 2 to 3 million dollars), calendering is the most economical method for producing thick PVC film and sheeting. Film and sheeting of the middle-gauge range between 3 and 25 mils is almost entirely produced by calendering. Today's calender lines are designed with throughput capacities of from 2,000 to 10,000 pounds of compound

per hour, or 70 - 100 yards per minute.. Widths of film and sheet usually run to 72 inches, with some as wide as 92 inches.

Because calender fabrication is economical only if the production volume is high, only a few end users can use the calendering process. The main products made on calender equipment are: vinyl sheeting, coated vinyls, and floor tile. Coated fabrics are widely used for upholstery. Unsupported vinyl film and sheet is used to manufacture inflatables, footwear, purses, handbags, wallets, raincoats, tablecloths, shower curtains, luggage, and other similar products. Over 90% of the PVC-coated fabrics used in furniture upholstery are produced by calendering. Only a relatively small quantity of high-style, "expanded vinyls" is cast from plastisol (see section below). In these products, the vinyl is foamed to give it a "hand" that is similar to leather. Expanded vinyl products can be made either by the casting or calendering process.

Most motor vehicles today use vinyl-coated fabrics as the primary upholstery material. The backing material is largely cotton. About 85% of these coated fabrics are made by the calendering process and the remainder by the casting or knife-coating process. Unsupported vinyl sheet also is used in a variety of automotive applications such as Landau tops and panel coverings. Crash pads are covered with a calendered sheet that is made from a blend of ABS and PVC. These products typically contain about 35% PVC, although some may contain as much as 70% PVC.

While the major application for vinyls in home furnishings is upholstery, the second largest application is wall covering. The wall covering product consists of PVC film laminated to paper, cotton, or other backing material. Window shades are frequently made from vinyl sheet. Light-gauge, clear, rigid, and semi-rigid PVC film is used in the manufacture of prefinished plywood and particle board. In this method, clear film is printed with a wood grain pattern and laminated to the board with the print on the inside. The prefinished product is used to manufacture such items as office furniture and stereo cabinets.

Rigid PVC films and sheet

made by the calendering process are also used extensively as surface finishes for construction products. For example, large quantities of gypsum board are finished with printed, embossed, opaque sheet which is adhered to the surface to yield a decorative and abrasion-resistant finished panel.

For the most part, calender operators buy raw resin and carry out the compounding in their own facilities. Homopolymer made either by suspension or bulk polymerization process is used to make these compounds.

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